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Using polysaccharides for the enhancement of functionality of foods: a review

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Abstract

Background: Flavor, taste and functional ingredients are important ingredients of food, but they are easily lost or react during heating and are not stable. Carbohydrate-carbohydrate interactions (CCIs) and carbohydrate-protein interactions (CPIs) are involved in a variety of regulatory biological processes in nature, including cell differentiation, proliferation, adhesion, inflammation and immune responses. Polysaccharides have high molecular weights and many intramolecular hydrogen bonds, can be easily modified chemically and biochemically to enhance bioadhesive and biostability of tissues. Therefore, polysaccharides are the foundation for building complex and stable biosystems that are non-toxic with highydrophilicity and easily biodegradable.

Scope and approach: In this review, we summarize the principles and applications of polysaccharide delivery systems in a variety of foods.

Key findings and conclusions: This review focuses on the self-assembly of carbohydrates with complex structures and discusses the latest advances in self-assembly systems. The host-guest complexes formed by polyvalent sugar conjugates have the potential to provide, control or target delivery or release systems. They can also extend the shelf life of food and prevent oxidation and isomerization during food storage. Moreover, very few studies have outlined a comprehensive overview of the use of various types of food polysaccharide matrixes for the assembly and protection of food ingredients, which is a very important area for further study.

Keywords： Polysaccharide, self-assembled, food functional ingredients, nanoparticles, directional delivery, bioavailability

1. Introduction

Nanostructured carbohydrates with self-assembly capabilities are used in both drug delivery and functional foods due to their good biocompatibility (Santiago & Castro, 2016). Carbohydrates with different shapes, sizes and structures can achieve different self-assembly strategies, resulting in food with abroad range of applications and functions. One of the methods utilizing interactions between bioactive molecules and carbohydrates is the creation of a larger functional unit by multiplexing multiple components under a variety of weaker (non-covalent) interactions. However, the weaker chemical bonds may also be destroyed under thermal or mechanical stress, so the chemical bonds are sometimes reinforced by covalent bonding to enhance the nanostructures. Most bioactive molecules in food are often water-soluble with poor bioavailability, reactivity, and stability after processing, storage and digestion through the human gastrointestinal tract. It is therefore important to provide an appropriate protective carrier and targeted transport material for the food active ingredient. The carrier matrix should first be food grade, biodegradable and have the ability to withstand harsh processing, storage and directional distribution. Carbohydrate is an important component of food, providing energy and remaining the function integrality of organs. Most carbohydrates are biocompatible within the human body and have good biodegradability, and they can meet the required carrier functional properties using only specific treatments (Fathi, Martin, & McClements, 2014).

Polysaccharides usually alter the food matrix to cause changes in rheological properties, which increases water retention and gel formation , leading to thickening of the food matrix. Other applications include the stabilization of foam, emulsion and

suspended particulate materials, improving palatability, preventing or reducing the formation of ice crystals in frozen foods and interacting with other biomolecules. The viscosity of food has a strong correlation with flavor perception. Highly sticky foods delay the release of food flavor and taste compounds. Thus, the appropriate polysaccharide-binding emulsifier formulation can effectively solve the problem of flavor loss. Currently, many food flavor manufacturers are also seeking polysaccharide-based formulations to improve the product's flavor quality and sensory experience. Biocompatibility and biodegradability are key factors for the polymer in the product design when used as a bioactive compound carrier. Natural polysaccharides, such as non-toxic and biodegradable polymer materials, have been widely used in the preparation of biological nano-carriers. The wide range of sources, good biocompatibility, non-immunogenicity, and the large number of modifiable functional groups render natural polysaccharides a good choice as bioactive nano-carriers. Moreover, natural polysaccharides degrade into oligosaccharides and can easily be absorbed without inducing inflammation. Because the structures of polysaccharides in whole grains, whole-wheat bread/pasta, brown rice, fruits and vegetables are complex and resistant to digestive enzymes, they require long digestion and absorption times. Therefore, it is necessary to alter the carbohydrate carrier's structure to control its solubility, digestion, absorption, specific release, and even targeted delivery to protect nutrients and bioactive compounds (Shibakami, Tsubouchi, Sohma, & Hayashi, 2015). Self-assembly is not a new concept in food sciences; thickened polysaccharides or gelation in sauces and puddings are good examples. The assembly can be performed by adjusting the

environmental conditions (i.e., temperature, pH, ionic strength, specific substances or ions), processing conditions (i.e., different external forces), or the concentration of molecules/particles in the system. The assembled structure depends on the physical and chemical properties as well as the nutrients and quality of the final products. A high-molecular-weight carbohydrate complex has a chain structure, and its diameter is at the nano-level. Such a complex can interact with other food compounds to initiate self-assembly in the presence or absence of external forces to minimize the Gibbs free energy of the mixture. This process requires a balance between repulsive and attractive forces to achieve thermodynamic equilibrium. The uniqueness of carbohydrates, due to their various polarities and charged groups, can therefore be used as carriers to bind or capture a large number of bioactive molecules with targeted delivery properties.

Most bioactive compounds are limited by poor solubility (e.g., curcumin extracted from turmeric), but some complex polysaccharides can be soluble in water. Polysaccharide carbohydrates can interact with most bioactive compounds through their functional groups, thereby retaining various hydrophilic and hydrophobic bioactive ingredients and increasing their bioavailability and solubility. The bioactivity of a nutrient is easily destroyed during passage through the GIT digestion, resulting in failure to achieve the effective concentration in the plasma and tissue. However, polysaccharides have a uniquely slow intestinal digestion rate, which is beneficial for the release of bioactive compounds. More interestingly, the protective effect can be significantly enhanced by a cascaded polysaccharide self-assembled package. Moreover, the stability of carbohydrates at high temperatures is beneficial for the protection of bioactive

components (Azuma, et al., 2014).

2. Carbohydrate-based self-assembled nanostructures

Chemical complementarity, structural compatibility and weak or covalent interactions create bonds between the self-assembly building blocks to form a hierarchical structure with different specific functions. The self-assembled structures and nanostructures can be subdivided according to their size and phase. Nanoparticles are usually divided by size into zero-dimensional, one-dimensional, two-dimensional and three-dimensional nanoparticles; according to phase, they can be divided into single-phase, multi-phase and complex-phase nanoparticles. Most carbohydrates in food are one-dimensional. One-dimensional nanostructure with a higher surface area can be self-assembled by electrostatic spinning, which in turn contributes to higher embedding rates (Rezaei, Nasirpour, & Fathi, 2015). A hydrogel is another means of forming an assembled structure. Hydrogels can form strong gels via physical cross-linking at the appropriate pH or temperature. Adding bioactive molecules (such as polyphenols or flavor compounds) to a three-dimensional network can help solve the problem of delivery of the bioactive to a specific location within the body (Shewan & Stokes, 2013). The combination of xanthan gum-based hydrogels and multifunctional carbohydrate colloidal nanofibers is an example of this type of structure (Gökmen, et al., 2015).

Two-dimensional self-assembled nanostructures include thin film coatings, laminates, and nanocomposites, which can be easily formed by interactions based on the local self-assembly of carbohydrate three-dimensional micelles. Micelles are invisible molecularly ordered aggregates in a solution formed by a number of solute molecules or

ions with hydrophobic groups as the core and hydrophilic groups as the shell. Amphiphilic polymers are macromolecules with both hydrophilic and hydrophobic chains in the same molecular chain of polymers. Amphiphilic polymers are usually copolymers formed by blocking, grafting or other methods. The hydrophilic and hydrophobic groups are mutually incompatible with each other and prone to micro-phase separation; thus, they reduce the surface tension of the solution. The formation of amphiphilic polymer micelles is a spontaneous process of minimizing the contact area between the hydrophobic chains and the aqueous solution. Due to intermolecular forces, such as hydrophobic interactions, electrostatic interactions, hydrogen bonding, and the solvent hydrophobic accumulation effect, the hydrophobic region forms a core, and the shell is wrapped by the hydrophilic chains formed outside the core, which stabilizes the micelles in solution. The main driving force of micellar formation is the free energy reduction of the system due to the attraction between the hydrophobic chains and the repulsive force between the hydrophilic chains to hydrophobic chains. Polymer micelles are prepared by a molecular self-assembly method. This method does not involve any organic solvents, such as emulsifiers or surfactants, and thus reduces the toxicity of the carrier. Moreover, the self-assembly method is a simple and spontaneous process in which molecules or subunits form a supramolecular structure without additional energy input. This type of method includes direct hydrolysis, ultra sonication, dialysis methods and solvent evaporation. The method chosen for a specific case depends on the dissolution and swelling ability of the polymer in water. Direct hydrolysis and ultrasonic methods are usually applied to water-soluble polymers or polymers with good swelling properties; dialysis or solvent

evaporation methods are usually applied to polymers with poor water solubility, such as nano-bio complexes composed of chitosan and cellulose with covalent bonds. Layer-by-layer assembly is an important technique for the development of nanoscale three-dimensional structures. Negatively charged polyanions and positively charged polycations are assembled layer by layer by electrostatic attraction. This is an emerging technology in the food industry and can effectively encapsulation to protect color and flavor substances and prevent the collapse of food structures. For example, biopolymers composed of xanthan gum and galactomannan through non-ionic interactions can extend epidermal growth factor (EGF) release time by 5-fold (Kaminski, Sierakowski, Pontarolo, dos Santos, & de Freitas, 2016). The following sections summarize the advances in delivery systems based on carbohydrates from variable biosources (Fathi, Martín, & McClements, 2014).

3. Plant-based carbohydrates

3.1. Starch

Starch and its derivatives have become the most studied and most popular polymer materials for use as active carriers. The size of natural-origin starch varies between 1 and 100 μm. Amylose consists of glucose units with α-1,4 glycosidic bonds while amylopectin consists of main chains linked by α-1,4 glycosidic bonds and side chains linked by α-1,6 glycosidic bonds. The process of spherulite formation in starch is the result of self-assembly, which produces starch nanoparticles. One assembly method involves inducing the encapsulation of fatty acids by amylose or other surfactants, followed by a combination of both to produce a supramolecular amylose spiral complex.

Sodium dodecyl sulfate (SDS), polysorbate 80 (Tween 80) and sorbitan monooleate (Span 80) can be used to control the size and surface morphology of starch nanoparticles to ensure the production of ultrafine nanoparticles with great thermal stability and dispersion. This process can be generated by mechanically assisted processing, such as ultrasonic, extrusion, autoclaving, or enzymatic treatment and acid hydrolysis (Xiaojing Li, et al., 2016). The starch nanoparticle complex can help self-assemble the insoluble small molecules together with the soluble protein through electrostatic interactions to form a nanoparticle carrier delivery system for loading the insoluble functional food ingredients (Bhopatkar, et al., 2015). The starch and its derivatives of the polymer micelles are generally formed by ultrasound and dialysis methods. Initially, an ultrasonic method is used to dissolve a starch-based polymer in an aqueous solution, followed by an ultrasonic method to disperse it evenly in the aqueous solution and to form micelles through intermolecular hydrophobic interactions. The size of the micelles can be controlled by the duration of the ultrasonic treatment. While this method is simple, the stability of the micelles is unsatisfactory. The dialysis method involves first dissolving hydrophobically modified starch in a solvent that is mutually soluble with water, such as dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF) or tetrahydrofuran (THF), followed by dialysis in water. Polymer micelles self-assemble to form micelles as the organic solvent is dialyzed away. The size, dispersibility and yield of the polymer micelles are related to the organic solvents. Micelles formed by this method are usually of small size and great dispersibility.

3.1.1. Formation of starch crystals

Another avenue with good prospects is targeting the release and delivery of bioactive molecules with starch as the matrix under specific controlled conditions. In particular, amylose can also form clathrates with various molecules, such as volatile flavor compounds or fatty acids. Amylose spikes can also be formed by amylose and guest molecules through non-covalent interactions. These amylose spikes have a strong tendency to self-assemble into supramolecular structures via helix-helix synergism.

Other spherulites are mainly composed of amylose and lightly branched starch polymers formed by "high-temperature regeneration". The long-chain amylose is concentrated along the radial direction of the spherulites, and the short-chain amylose is concentrated along the tangential direction of the spherulites. These two types of prepared starch can decrease the digestion rate or increase resistance to enzymatic digestion. The digestion rate depends on the self-assembly morphology and surface characteristics: a dense and smooth surface is not conducive to decomposition by digestive enzymes (Fig. 1) (Kiatponglarp, Rugmai, Rolland-Sabaté, Buléon, & Tongta, 2016).

3.1.2. Chemical modification

Starch molecules contain large numbers of hydroxyl groups, which makes them hydrophilic. However, the solubility of starch in cold water is quite poor, mainly due to the easy formation of hydrogen bonds among hydroxyl groups. Therefore, the physical and chemical properties of natural starch limit the application of starch in many foods. Chemical modification linking hydrophobic and hydrophilic groups can adjust the self-assembly of starch and thus overcome these limitations. Hydrophobic modification is mainly achieved through an esterification reaction, which not only destroys the

intermolecular hydrogen bonds to improve the solubility but also makes the starch amphiphilic. Because starch exhibits bioactivities, including anti-inflammatory, anti-viral, nontoxigenic and non immunogenic, with very good biocompatibility, and biodegradability, starch and its derivatives are now considered ideal materials for the preparation of biological nano-carriers and are commonly used to encapsulate insoluble bioactive molecules. Modifications mainly improve the physical and chemical properties of the hydroxyl, hydrophilic or hydrophobic groups of starch through grafting, esterification and etherification. Self-assembly in an aqueous solution can easily form micelles and polymer vesicles (Fig. 2) (Marefati, Sjöö, Timgren, Dejmek, & Rayner, 2015).

For example, hydrophobically modified octenyl succinic anhydride (OSA) starch derivatives are most widely used for encapsulating volatile perfumes. The function of OSA starch is primarily based on steric hindrance, which preferentially moves to the gas/water interface when dissolved in water. The hydrophilic carboxyl groups extend into the aqueous phase, while the lipophilic octenyl chains extend into the oil phase; the interface tension of the OSA starch in the oil/water interface through the hydrophobic octenyl action is lower compared to other starch derivatives, which helps form a continuous boundary layer and greatly enhances intermolecular cohesion (Wang, Yuan, & Yue, 2015). The increase in the degree of substitution (DS) and the decrease in the critical concentration at the time of embedding contribute to the decrease in the size of the starch nanospheres and the formation of nanospheres with spherical and/or sharp edges encapsulating the hydrophobic substance resulting in strong stability (Gu, Li, Xia,

Adhikari, & Gao, 2015).

3.1.2.1. Grafted starch polymer micelles

There are two types of grafted polymers: one consists of a hydrophobic backbone and hydrophilic side chains, and the other consists of a hydrophilic backbone and hydrophobic side chains. Both grafted polymers can more easily form a core-shell structure micelle with one chain directed inwards and the other chains directed outwards in the aqueous solution through self-assembly compared to the block polymer. The size, structure and properties of the grafted polymer micelles can be effectively controlled by the configuration of the polymer, the length and number of side chains and the grafting points. Therefore, it is usually easier to synthesize amphiphilic grafted polymers than block polymers. The grafted starch-based polymer micelles are mostly chemically modified by esterification and etherification. Hydrophobically modified starch can be used as a self-assembled biopolymer for the protection of insoluble bioactive substances.

3.1.2.2. Block starch polymer micelles

Two or more polymers of different compositions and properties are linked by chemical bonds to form a block polymer, and the large number of reactive hydroxyl groups in starch molecules contributes to the introduction of a block polymer. The amphiphilic starch-based polymer has both hydrophilic and hydrophobic chains. When it is placed in a solvent with different dissolution abilities for each type of chain, the polymer can be self-assembled in an aqueous solution due to a large difference in solubility, forming a polymer core with a unique core-shell structure, and the hydrophobic groups in the aqueous environment can aggregate into the core and are surrounded by the

hydrophilic chains.

Currently, the methods for making amylose-derivative block polymers mainly include the enzymatic polymerization method, the coupling method and the active/controlled polymerization method. The latter two methods are research hotspots. Enzymatic polymerization utilizes maltooligosaccharide as a substrate and phosphorylase to catalyze the polymerization of the glucose-1-phosphate monomer to make amylose block polymers. This method, while it can control the molecular weight of the starch chain very well is complicated. The coupling method requires the protection of hydroxyl groups in the high-molecular-weight starch, followed by degradation to obtain low-molecular-weight amylose derivatives with reactive functional groups. Finally, coupling reactions among the functional groups result in block polymers, which are biodegradable and can be degraded by α-amylase. However, this coupling method is still cumbersome.

The active/controlled polymerization method is the most efficient and simplest method for the synthesis of amphiphilic block polymers. In this method, click chemistry is the main reaction, including the metal ion-catalyzed cycloaddition of azides and alkynes and a condensation reaction between aldehyde and aminooxy groups. In the presence of an active hydrogen compound, ε-caprolactone is prone to polymerization. The poly (ε-caprolactone) (PCL) is then grafted to the backbone of maltose by click chemistry. The size of the nanoparticles can be reduced with a decrease in the molecular weight of PCL or an increase in the number of hydrophilic groups (Isono, et al., 2016).

3.1.2.3. Polyelectrolyte starch polymer micelles

Micelles that are formed in water-soluble block polymers in an aqueous solution by electrostatic interactions, hydrogen bonding or metal coordination are usually defined as polyelectrolyte micelles. In this process, hydrophilic polymer chains self-assemble to form a tether-like fence and wrap around the outer layer to maintain the spatial stability of the micelles. The core is formed by the aggregation of part of the polymer blocks, which is the result of intermolecular forces (hydrophobic interactions, electrostatic interactions, metal complexation and hydrogen bonding between block copolymers). For example, hydrophobic apogossypolone (ApoG2) and hydrophilic adriamycin (doxorubicin, DOX) both have good anti-tumor activity; if they are loaded into nanoparticles made of different suitable materials, they can be absorbed by human cells or tissues due to their different sustained-release characteristics to achieve the best combination of treatments. Starch first grafts to stearic acid, which is catalyzed by glycidyltrimethylammonium chloride (GTAC) to synthesize cationic stearic acid-grafted starch (CSaSt). This CSaSt amphiphilic conjugate can easily encapsulate ApoG2 to form amphiphilic starch micelles (AAST MCs) during self-assembly. Subsequently, DOX is adsorbed to excess hyaluronic acid (HA) nanoparticles (DHA NPs) through electrostatic interactions. Finally, DHA NPs with 8-9 negative charge units, assemble with AAST MCs a positively charged unit by electrostatic interactions to produce mulberry-like bicomponent nano-carriers (MLDC NCs). The therapeutic dose of this two-component delivery system *in vitro* and *in vivo* is only one-fifth that of the non-carrier two-component combination and can be used for targeted therapy to the tumor (K. Li, et al., 2015).

3.2. Cyclodextrin

Cyclodextrin (CD) is an enzymatic product of amylase and is included in the US Food and Drug Administration's (USDA) list of products generally recognized as safe (GRAS). The most common natural α-, β- and γ-CD contain 6, 7 and 8 D-(+)-glucopyranose units, respectively, bound by α(1-4) glycosidic bonds. CD with more than eight glucose units also exists; however, it is extremely difficult to generate and purify in the real environment. CD contains a relatively hydrophobic internal cavity structure, which can form complexes with a variety of molecules, including fat, flavor substances and pigments, through molecular self-assembly. The appropriate complex molecular size can result in greater connection strength. Therefore, CD is widely used to protect fragrance or unstable flavour compounds of food formulations in harsh environments during food processing, storage and delivery.

Because CD contains primary and secondary hydroxyl groups, the surface of CD is hydrophilic, which can effectively promote the conversion of complexed volatile matter from gas or liquid phase into powder. The encapsulation of CD and guest molecules is affected by many factors, including size, geometry and electrical properties. Size refers to the match between the CD cavity and the corresponding guest molecule. The geometry and the stereogenic effect of the guest molecule can also affect the complex, and furthermore, due to the highly hydrophilic effect of ionic guest molecules, they can only form a weak complex with CD, while weakly polar guest molecules can complex with CD more strongly (Jahed, Zarrabi, Bordbar, & Hafezi, 2014). Because of these unique structures and properties, CD can be widely used in the construction and regulation of aggregates in supramolecular self-assembly.

CD can also be used to protect against oxidative degradation and heat- and light-caused decomposition of edible flavors and bioactive substances. β-cyclodextrin has been found to be an effective aromatic compound retention agent during the heat treatment process due to its relatively suitable cavity volume (Kfoury, Auezova, Greige-Gerges, & Fourmentin, 2015). β-cyclodextrin is also widely used because it is reasonablely priced (Celebioglu, Kayaci-Senirmak, İpek, Durgun, & Uyar, 2016). In addition, cyclodextrin can effectively prevent enzymatic oxidation caused by polyphenol oxidase or phenolic compounds in fruit juices by non-covalent interactions with polyphenol oxidases (Aguilera, et al., 2016).

CD preserves food aromas and flavors and controls their release during storage and consumption, improving the solubility and retention of these insoluble substances. The encapsulation of cyclodextrins also enhances the stability of fragrance and taste, prolongs the shelf life of products, protects products from isomerization and oxidation during storage, and creates a controlled release system for active substances. Cyclodextrin inclusions are also used to change food flavors; eliminate food bitterness and odors, such as the deodorization of soy milk, soy protein and some fish and rice; and the unpleasant spicy or bitter (Preis, Grother, Axe, & Breitkreutz, 2015) effects of curcumin in food and medicine. β-cyclodextrin is also used as a cholesterol chelator for livestock products (such as egg yolk, milk, butter, lard, cream, and cheese), which can reduce cholesterol by 87.54% (Lamas, et al., 2016) in β-cyclodextrin-egg cross-linking derivatives to improve its quality (Y. Li, Chen, & Li, 2017). β-cyclodextrin can also be used to replace egg yolk in bread to maintain its physico-chemical and sensory properties during storage (Marcet,

Paredes, & Diaz, 2015). Another application of CD is in the design of nano-bioactive food packaging materials. CD can be incorporated as a fragrant seasoning, a bacteriostatic substance or a bioactive agent, which allows it to be gradually released into food to maintain the sensory nature and to prevent the growth of microorganisms. The slow release of carvacrol in packaging is a good example (Lavoine, et al., 2014).

Emulsions are highly valuable because they are widely used in food, pharmaceuticals and cosmetics. Stabilized emulsions are usually obtained by adsorbing surfactants, polymers, or particles at the liquid-liquid interface to inhibit emulsion delamination, flocculation and coalescence. Recently, CD has been used as a substitute for traditional surfactants in emulsion stabilization. In contact with oil components, CD can form amphiphilic supramolecules at the oil/water interface with oil molecules via self-assembly. This supramolecule has a surface activity that can significantly reduce oil/water interfacial tension. Oil-CD inclusion complexes (ICs) are connected to the surface of the emulsion droplets by means of CDs in the aqueous phase. The particles formed by CD and oil are distributed on the surface of the oil droplets. These ICs can further grow into microcrystals and produce dense layers that adhere to the surface of emulsion droplets, similar to Pickering emulsions (solid particle-stabilized emulsion), which can stabilize emulsions. Compared to surfactant-stabilized emulsion, the stability of Pickering emulsions is less affected by pH, salt and temperature and results in none of the environmental pollution or toxicity problems associated with other surfactants. Sometimes, CD and a surfactant are added together through interfacial diffusion, adsorption and rearrangement to form more stable emulsions with various configurations

379 (Fig. 3) (H. Xu, Liu, & Zhang, 2015). However, not all surfactants can stabilize emulsions
380 as the type, amount, and initial position of a surfactant can all affect their stability (Xue Li,
381 et al., 2014).

382 Natural cyclodextrin has limited bonding capacity and is even unstable in certain
383 circumstances (i.e., a strongly acidic environment). In particular, the solubility of
384 β-cyclodextrin in water and other solvents is not high, which limits the application of
385 cyclodextrin. Therefore, it is necessary to modify the structure of cyclodextrin and
386 synthesize cyclodextrin derivatives that can effectively overcome these challenges.
387 Common cyclodextrin derivatization methods include alkylation, acylation, amination,
388 silylation and azide. Cyclodextrin contains three different types of hydroxyl groups,
389 located at C2, C3 and C6, pointing to two different directions of the cyclodextrin
390 molecular ring structure. The reactivity of each hydroxyl group varies under different
391 reaction conditions and results in distinct substitution products. Table 1 lists the assembly
392 objects and methods, basic properties of common starch and cyclodextrin and its
393 derivatives, and their recent applications in food science.

394 *3.3. Inulin*

395 Inulin is a fructose polymer linked by β-(1-2)-D-fructofuran, and the length of the
396 fructose chain varies from 2 to 60 monomers. The main function of inulin is the storage of
397 carbohydrates in most plants (Apolinario, et al., 2014). Inulin has a variety of nutritional
398 functions, including immune activity, hypolipidemic effects, prebiotic effects (affecting
399 intestinal microbiota), and stimulation of the absorption of minerals (calcium and
400 magnesium). The self assembly of inulin particles has been widely studied in comparison

401 to glucan and fructans and it has been shown that the functionality of inulin has great
402 potential for further study. The precipitation of inulin initiates from interactions among
403 hydrogen bonds between adjacent chains and assembly from random coils to a helical
404 one-dimensional conformation. The helical conformation grows into a secondary structure
405 due to the interaction between glucose at one end of the inulin chain and fructose on the
406 adjacent chain. Subsequently, the tertiary structure of inulin is formed via cross-linking of
407 every five hydrogen bonds and two-dimensional semi-nano crystal layers (Fig. 4)
408 (Barclay, et al., 2016). Both the degree of polymerization and the process have a large
409 impact on the physical and chemical properties of inulin. The furanosyl content of inulin
410 is smaller and more flexible than that of glucan dextran, and the backbone structure has
411 higher molecular elasticity and hydrophobicity and, therefore, relatively low glass
412 transition and melting points relative to other oligosaccharides and polysaccharides.
413 However, unlike the other sugars described above, inulin cannot be metabolized by the
414 human body, which favors it for some unique and positive attributes, such as metabolic
415 utilization by the kidney and beneficial colonic bacteria such as lactobacill and
416 bifidobacteria. Inulin is more suitable as a food adhesive than glucose or lactose due to its
417 reduction groups (Mensink, Frijlink, van der Voort Maarschalk, & Hinrichs, 2015). With
418 an increase in inulin polymerization, the glass transition temperature (*Tg*) of inulin also
419 increases, but the degree of polymerization of the self-assembled natural inulin active
420 compound does not have an impact on *Tg* or the retention of embedded substances. The
421 particles formed by embedded substances with high DP after drying are of low moisture
422 and can help improve the stability of emulsions after re-dissolution (Silva, Zabot, Bargas,

423 & Meireles, 2016). However, the ability of natural inulin as a single packaging material
424 for self-assembling hydrophobic active compounds is limited. Therefore, it is important to
425 combine natural inulin with other low-calorie biopolymers (such as maltodextrin,
426 modified starch, chitosan, protein or gum) to improve the rate of interfacial adsorption;
427 thus, the wall material can have the dual function of prebiotic functional characteristics
428 and self-assembling embedding ability (Dima, Pătrașcu, Cantaragiu, Alexe, & Dima,
429 2016). In addition, inulin can be self-assembled after hydrophobic modifications and
430 provide a more useful function. The resulting derivatives can be used as suitable
431 aggregators and stabilizers of emulsions, and they can effectively encapsulate and deliver
432 water-insoluble active compounds in food, pharmaceutical or cosmetic products. Table 1
433 lists common inulin assembly objects, the basic nature of the method and recent
434 applications in food science.

435 *3.4. Cellulose*

436 Cellulose is the most abundant polysaccharide in nature and includes hundreds to
437 thousands of straight-chain β-(1→4)-linked D-glucose units. Although the amount of
438 cellulose is vast, humans consume only a small amount of it because it is difficult to
439 digest, making it mainly a nutritional source for animals. Nevertheless, due to the wide
440 range of sources of cellulose, scientists are still working on developing products utilizing
441 cellulose that are acceptable for both ruminant and non-ruminant animals.

442 At present, the most widely used celluloses in the food industry are microcrystalline
443 cellulose and bacterial cellulose. They are non-toxic, tasteless, and safe and have unique
444 physical and chemical properties which do not affect product quality, and they can be

445 used as food additives, such as emulsifiers, thickening agents, foam stabilizers, or
446 nutritional fortifiers or food packaging materials to make cellulose films. Microcrystalline
447 cellulose is used in dairy products for thickening and gelling the water phase in an
448 oil-water emulsion, to prevent the aggregation and combination of oil droplets and thus
449 stabilize the suspension. Cellulose is a dietary fiber, and the cellulose self-assembly
450 strategy is harnessed mainly to improve its functional applications. However, the rigid
451 molecular chain structure and the formation of hydrogen bonds result in insolubility in
452 common solvents. Therefore, there are relatively few studies on the direct hydrophobic
453 modification of cellulose as a hydrophilic skeleton. However, recent studies have shown
454 that interactions between amphiphilic and hydrophobic parts of unmodified cellulose play
455 an important role in determining the crystal structure and solubility of cellulose, which
456 allows hydrophobic modifications at low temperatures in organic, acidic, or alkaline
457 solvents. The hydrophobic modification of cellulose in food is usually a necessary
458 condition for maintaining the stability of the emulsion, which produces amphiphilic
459 cellulose or cellulose derivative-based polymers. These amphiphilic polymers can
460 self-assemble into nanoparticles, which is one type of grafting method. The factors that
461 can impact on self-assembly include the cellulose skeleton length, hydrophobic chain
462 length and density, concentration, polarity, temperature and pH of the solution.
463 Nanocrystalline cellulose is usually used to stabilize emulsions; the amphiphilicity of
464 cellulose crystallization allows it to assemble layer by layer and stabilize the emulsion
465 through the Pickering mechanism. Over the past few decades, dissolvable and
466 regeneratable forms of cellulose have been extensively studied to improve the enzymatic

467 hydrolysis rate of cellulose. In the regeneration step, phosphoric acid is often used to
468 remove the solvent (water) from the cellulose molecule allowing cellulose to
469 self-assemble into nanostructured cellulose. Moreover, some species of bacteria can also
470 biosynthesize cellulose nanocrystals using glucose as the substrate (Dayal & Catchmark,
471 2016), but the method has proven difficult to commercialize thus far. Nanostructured
472 cellulose plays an important role in flavor delivery (Hao, et al., 2015). Electrostatic
473 technology can also effectively assist cellulose in assembling functional substances
474 (Rezaei, et al., 2015). Table 1 lists the basic properties of cellulose, methods for its
475 assembly and recent developments in its application in food science and industry.

476 *3.5. Pectin*

477 Pectin is an important food gelation agent that is most commonly found in the cell
478 wall of terrestrial plants. Pectin is composed of a number of α-D-(1→4) galacturonic acid
479 residues through linear linkage. DE (degree of esterification) is an important factor in
480 characterizing the esterification of the carboxyl and methanol groups of pectin. DE is the
481 ratio of the esterified GalA groups to the total GalA groups, and the DE value of pectin in
482 general ranges from 60% to 90%. Pectins with a DE value greater than 50% are known as
483 high-methoxy pectins (HM pectins), and pectins with DE value less than 50% are known
484 as low-methoxy pectins (LM pectins). LM pectin can be further subdivided into two
485 categories: amidated LM and conventional LM pectin. LM pectin has the characteristics
486 of anti-hydrolysis on oral, gastric and intestinal microbial-specific enzymolysis. Therefore,
487 it can be used as an effective carrier for bioactive substances that are sensitive to acids.
488 However, as a protective carrier, its solubility is often high.

The hydrogen bonding and hydrophobic interactions are the main forces driving the aggregation of pectin molecules. For pectin molecules in the neutral or slightly acidic, most of the unesterified carboxyl groups are present in the form of ionized salts and this causes repulsion between negative charges preventing pectin from forming a network. This scenario also reduces the attractive forces between pectin and water molecules and the repulsive forces between pectin molecules. However, LM pectin requires calcium (or other polyvalent cations) for proper gel formation. The affinity and the capability of divalent cations to form a gel can be ranked as follows: barium> strontium> calcium. The mechanism of LM pectin gelation is well known as the "egg box" model. GalA monomers in a specific sequence of galacturonic acid in adjacent chains are interlinked by electrostatic and ionic bonding through carboxyl groups. A large amount of sugar (i.e., 60% or higher) forms hydrogen bonds by dehydration to reduce gel formation. Many studies have added calcium salts and LM pectin (to increase the binding capacity of pectin to calcium) to matrix tablets to delay the release of embedded substances (Fig. 5a and 5b) (Sriamornsak, 2011). Gel beads are formed by LM pectin with calcium, which can cross-link to form a poly-Gal chain. Pectin beads are produced by ionic gel preparation and often perform as a delivery system for the sustained release of active materials. However, their release *in vitro* is usually accelerated. By changing the LM pectin DE, the calcium pectin gel beads can be changed and the release mode can be modified.

Therefore, scientists often follow several strategies to develop pectin-derivative carriers. First, pectin needs to be biodegradable by bacteria and highly soluble. An

511 alternative is to allow interactions between functional components and pectin molecules
512 to modify the local structure, for example, electrostatic interactions with proteins (such as
513 lactoglobulin) to form 150-500 nm nanoparticles and then become a delivery system for
514 active substances, including ω-3 unsaturated fatty acids and others (Jones & McClements,
515 2010; Zimet & Livney, 2009). A polyelectrolyte complex (PEC) is formed by electrostatic
516 interactions between the polymer electrolytes and their counterparts with opposite charges
517 in aqueous solution. The structure of pectin contains many carboxyl groups, thus allowing
518 pectin to interact with the oppositely charged membrane or liposome. Self-assembled
519 pectin-liposomal nanocomposites (PLNS) can be prepared by simple mixing of a pectin
520 solution with cationic liposomes. The carboxyl group in galacturonic acid in pectin can be
521 methyl esterified or reacted with an ammonia group to form an amide group. The
522 esterification degree (DE) and amidation degree (DA) are important methods of pectin
523 classification. High-methoxylated pectin (CU201, 70% DE, 200 kDa), low-methoxylated
524 pectin (CU201, 38% DE, 80 kDa) and low-methoxylated amide pectin (CU020, 29% DE,
525 20% DA, 150 kDa) can interact with amine groups of liposomes (SA). AFM images show
526 a small amount of branched pectin and spherical liposomes (Fig. 5c) (Sriamornsak, et al.,
527 2008).

528 Changes in zeta potential and particle size are important factors for verifying the
529 success of liposome coating. The high charge density on the surface of liposomes
530 promotes the adsorption of pectin. Moreover, a high concentration of pectin with an
531 increase in the coated liposome size results in better coverage of liposomes. The increase
532 in the high-fat pectin ratio may be due to bridging flocculation. The appropriate ratio of

pectin can help produce stable monolayered liposomes and prevent bridging flocculation (Fig. 5d) (Alund, Smistad, & Hiorth, 2013).

Moreover, the interactions between pectin and a cationic solution environment can be used to change the gel properties to improve the embedding rate of functional substances. With an increase in the salt ion content, unlike the alginate gel, the number of bar-like interfaces decreases, while the number of dot-like crosslinks increases, and semi-flexible chains are also present (Fig. 5e and 5f) (Ventura, Jammal, & Bianco-Peled, 2013). Table 1 lists pectin assembly objects, the basic properties of the method and recent developments in the food industry.

3.6. Animal polysaccharides

3.6.1. Chitosan

Chitosan is mainly found in shells of shrimp and other crustaceans. Chitosan essentially consists of a large number of (1-4)-glycosidic bonds linking N-acetyl-2-amino-2-deoxy-d-glucopyranose (glucosamine) and 2-amino-2-deoxyd-glucopyranose. Chitosan is widely used in the food industry for its antibacterial, clarification, and deacidification properties and its mouth-feel. Moreover, chitosan can be used as a controlled release medium for antioxidants, nutrients, spices and drugs.

Chitosan's cations and hydrophobic sites make it a polyelectrolyte and amphiphilic compound. In acidic media, chitosan is highly protonated due to the positively charged amino chitosan groups. Moreover, both intramolecular and intermolecular hydrogen bonds (due to the presence of -OH single bonds and NH_2 single-bond groups in the chitosan backbone) contribute to self-assembly. The cationicity of chitosan is

advantageous for its incorporation into the surface of the anionic species by electrostatic forces and hydrogen bonding. Biopolymers with the opposite charge, such as alginates, pectins, xanthan gum, carrageenan, acacia and anionic lipids, can provide interesting nanostructures in delivery systems for various components. For example, the NH_3 groups of chitosan and the phosphate groups of modified lecithin can assemble via electrostatic interactions to deliver hydrophilic compounds. Nanoparticles show excellent stability at certain pH (3-6) and ionic strength ranges, and nanoparticles can be easily made into freeze-dried powders (Chuah, Kuroiwa, Ichikawa, Kobayashi, & Nakajima, 2009). A self-assembled complex of chitosan with α-lactalbumin or with β-lactoglobulin can also be used as potential delivery vehicles (Lee & Hong, 2009). Moreover, since the chitosan backbone has many functional groups, it can assemble better into nanomaterials after chemical modification to assemble active ingredients in food or drugs (Y. Yang, et al., 2014). The specific methods include the following: (1) the ionic cross-linking method. In an acidic medium, the amino group in the chitosan chain is easily protonated, so that it has a certain positive charge. Under certain conditions, chitosan with positive charges is mixed with anionic cross-linking agents (such as carboxylic acid or tripolyphosphate (TPP)) in aqueous solution, and the protonated amino group can interact with the anionic cross-linking agents to wrap the core materials to form chitosan-based nano-capsules. Cross-linking between TPP and low-molecular-weight chitosan can produce nano-capsules with an average particle size of 138 nm. Nano-capsules made using this method do not require organic solvents, and the cross-linking agent is of low toxicity. Therefore, this process is widely used to make sustained-release capsules, but the disadvantage is

577 that the particle size distribution is wide and the stability is poor (Fan, Yan, Xu, & Ni,
578 2012). (2) Layer-by-layer self-assembly method. This method is suitable for the
579 preparation of double- or multi- layer nano-capsules. The main principle is to use
580 easy-to-remove or need-to-be-covered nano-particles as a template and to alternately
581 deposit polyelectrolytes with different charges on the surface of nanoparticle. Finally, the
582 particles are removed to obtain nano-capsules. Liposomes are an artificial membrane with
583 targeted drug delivery properties. They have good biocompatibility, but their structure is
584 unstable and can be easily damaged by changes in external temperature and pH. To
585 improve the stability of liposomes, nano-lipid particles are wrapped in layers of chitosan
586 and alginate capsules by the layer-by-layer method, which not only improves the stability
587 of liposomes but also enhances their sustained release to a certain extent. This method not
588 only effectively controls the thickness of capsule shells but can also impart the directional
589 release properties of capsules through the introduction of various capsule wall materials
590 (W. Liu, Liu, Liu, Li, & Liu, 2013). (3) Re-coagulation method. In this method, core
591 materials are distributed into two or more packaging materials with different charges,
592 followed by interactions among packaging materials by the adjusting pH, temperature,
593 and concentration of the system, which results in a low-solubility complex that
594 precipitates to form nano-capsules. The nano-capsules are prepared on the surface of
595 carbon nanotubes by the re-coagulation method between chitosan and
596 ethylenediaminetetracarboxylic acid. This nano-capsule not only achieves the effective
597 coating of enzymes and some proteins but can also be used as a biosensor or bioresponder
598 (Fig. 6) (H. Liu, et al., 2013). Table 1 lists the assembly objects and methods of chitosan

599 and its recent applications in the food industry.

600 *3.7. Algae polysaccharides*

601 Acid polysaccharides are another specially constructed type of polysaccharide found
602 in seaweed, including fucoidans and laminarans in brown algae (Phaeophyceae),
603 carrageenans in red algae (Rhodophyceae), and ulvans in green algae (Chlorrigyceae)
604 (Wrigstedt, et al., 2010). Research into the delivery of active substances using acid
605 polysaccharides is ongoing (Venkatesan, Anil, Kim, & Shim, 2016). These
606 polysaccharides have a stronger ability to bind to proteins in self-assembly and therefore
607 are used in dairy and meat products. For example, the interaction between fucoidan and
608 bovine serum albumin at pH 4.0 through $–SO^{3-}$ and NH^{3+} favours the formation of
609 complexes with very dense and intimate internal structures; the complex can dissociate
610 into the soluble state in the presence of 0.01 M NaCl at pH 4.5 (D.-Y. Kim & Shin, 2015).
611 Moreover, the thermostability, solubility and emulsification around PI of complexes
612 prepared at high temperature can be improved (D.-Y. Kim & Shin, 2016). Moreover,
613 chitosan and fucoidan can form multilayered hydrated nanocomposites via electrostatic
614 attraction, which can further embed bioactive compounds. Carrageenan is another
615 polysaccharide gel widely used in the food industry, which can thicken and stabilize
616 liquids. Carrageenan can also bind strongly to food proteins. In an *in vitro* model,
617 carrageenan could bind to protamine to form carrageenan/protamine polyelectrolyte
618 nanocomposites (Dul, et al., 2015). Carrageenan can also interact with surfactants, the
619 cationic glycine betaine amide, of different concentrations to form multiscale nanoparticle
620 complexes, which can significantly reduce the electrostatic interactions between the

surfactant and the polymer and gradually dissociate the polymer nanostructures (Gaillard, et al., 2017). Alginate is another brown anionic acidic polysaccharide and is widely distributed in the cell wall of brown algae. Alginate is mainly composed of α-l-guluronic acid and β-D-mannuronic acid residues linked by 1,4-glycosidic linkages. Alginate can be combined with 200-300 times its own weight of water to form a sticky gel. The formed gel does not provide any nutrients, but it can stabilize the emulsion system. In the self-assembly process, alginate is often used as a base carrier and complexes with chitosan to carry flavors, such as capsaicin and other flavor substances. Chitosan/alginate self-assembles layer by layer to form a biofilm with an anti-fungal or anti-bacterial coating (F. Jiang, Yeh, Wen, & Sun, 2015). Table 1 lists the algae polysaccharide assembly objects, the basic methods and its applications in the food industry.

3.8 Applications in Biomedicine and Environment

Polysaccharides and their derivatives are superior to synthetic polymers because of their non-toxicity, biodegradability, compatibility and low cost. They are also widely used in biomedical and environmental fields, such as tissue engineering, biological imaging or environmental utilization.

Polysaccharides and their derivatives, applied in tissue engineering, are often used in biological signal transduction, cell adhesion, cell proliferation, cell differentiation, cell responsive degradation, re-modeling, regeneration or planning of the shape and structure of cell growth, etc. Sugar as a biological scaffold in tissue engineering can meet the requirements of bio-compatibility, non-toxicity, biodegradable rate, appropriate porosity and structural integrity (Khan & Ahmad, 2013).

Biological imaging is an important tool for understanding key physiological information and pathological processes, such as cancer detection and treatment, stem cell transplantation, immunogenicity and tissue engineering. Biological imaging has advantages in using fluorescence as signal output. Compared with small organic dyes, fluorescent nanomaterials exhibit excellent light stability, adjustable size emission, multi-functional potential and ideal pharmacokinetic behavior. An alternative luminescent nanometer material of (FONs) fluorescent organic nanoparticles type appeared recently. Chitosan is used to prepare ultra-small cross-linked chitosan nanoparticles by "one-pot" multi-component reaction or atom transfer radical polymerization (ATRP), the particles can show strong yellow or red color and have better water dispersibility (Wan, et al., 2016). β-cyclodextrin can be used to prepare red fluorescent organic nanoparticles with aggregation-induced emission（AIE）characteristics（FON）(D. Xu, et al., 2017)，or preparing an amphiphilic AIE active copolymer with strong green fluorescence through host-guest interaction (H. Huang, et al., 2017). Starch produces AIE active polymer nanoprobes with strong blue-green or green-yellow fluorescence through a "one-pot" strategy with pH and glucose responsiveness and good biocompatibility (internalization within 3 hours) (M. Liu, et al., 2015; Shi, et al., 2018). Oxidized sodium alginate (OSA) can be used to prepare probes with red fluorescent AIE activity (Wan, et al., 2017).

The pollution of heavy metal ions in the environment has become a serious environmental problem and can exist in the natural environment for a long time, thus creating long-term risks to ecosystems and human. Copper ion is the most typical of heavy metal ions because it is involved in electroplating, paint, electricity, fertilizers,

665 wood manufacturing and pigments. Many adsorbents with small size and high specific
666 surface area, including carbon nanotubes (CNT), magnetic nanoparticles, graphene oxide,
667 silica nanoparticles, etc. have been used. Chitosan is rich in amino, carboxyl and hydroxyl
668 functional groups and can be used as a coordination site. Carboxymethyl chitosan was
669 immobilized on CNT to form CNT-based chitosan nanocomposites by the combination of
670 mussel adsorption chemistry and Michael addition reaction, which could overcome the
671 shortcomings of traditional CNT (Zeng, et al., 2016).

672 **4. Summary and future trends**

673 Recent developments in healthcare products require the integration of new
674 technologies into customized functional food, which poses new challenges to food
675 scientists. The self-assembly strategy is an effective technique for the design and
676 manufacture of delivery agents for bioactive substances to effectively control interactions
677 among food ingredients. Self-assembly technology plays a vital role in nutritional and
678 functional foods because of the great variation in structural, functional and physical and
679 chemical properties. Self-assembly technology can be used to assemble existing
680 micro-components to form larger structural units, which requires the manipulation or
681 control of structures. The appropriate substrates, environmental conditions and chemical
682 or physiological functions must be identified in advance. Carbohydrates, especially
683 polysaccharides, are a very suitable base matrix due to their structure and special
684 functions. Self-assembly has proven to be an attractive technology for the delivery of
685 food nutrients and functional components. Additionally, the application of
686 nano-technology combined with self-assembly is the key to the manipulation of food

polymers to improve their functional structure, which can effectively improve the quality, feel, functional ingredients and shelf life of food. However, different monosaccharide structures are used as building units, including isomeric stereoisomers, sequence changes, side chain connection, branching and distribution, and modified functional groups leading to wide structural diversity of polysaccharides. More studies are needed to address the problem of assembly and stability to improve the functions of assembled complexes. Parallel to developments in the laboratory, computer simulation and theoretical modeling technology can also help solve key issues in the assembly process. More work on the biomedical applications of carbohydrates/polysaccharides and their biological behavior *in vivo*, including adsorption, distribution, metabolism and excretion is essential. This review explained recent developments in self-assembly strategies, behaviors and methods, which can provide a useful reference for further studies of carbohydrate carrier delivery systems. When designing a delivery system, more consideration needs be given to the requirements of the human body's internal environment, in order to adjust the system more intelligently. This may be an area for the future direction of development in this field.

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1110 Table 1 Recent studies regarding the use of polysaccharides matrix active compound
1111 delivery systems

Biopolymers	Modified solvent and assembly method	Potential objects	Main results	References
Starch	Octenyl succinic anhydride (OSA)	Highly moisture-sensitive substances	The encapsulation of bioactive compounds was achieved using a glass transition temperature of different amorphous phases in a phase separation array (hydrophobically modified starch and sucrose binary blend system).	(Tedeschi, Leuenberger, & Ubbink, 2016)
	OSA	Shea oil with liquid and solid	Powder filled with shea oil was prepared via the freeze-drying method using water-in-oil-in-water (W/O/W) double emulsions (Fig. 2). The stability after freeze-drying was enhanced by OSA-modified starch Pickering emulsions.	(Marefati, et al., 2015)
	OSA	Curcumin	Layer-by-layer (LBL) self-assembly: ultrasonic-aided chitosan (polycation) and Na-CMC (polyanionic) materials were continuously adsorbed onto the starch surface to form a stable curcumin nanoemulsion polymer multi-shell.	(Abbas, et al., 2015)
	Deoxycholic acid	Antitumor active drugs	Novel spherical nanoparticles with amphipathic properties; the average size of the aggregates ranged from 182 to 247 nm, with a good response to pH.	(J. Yang, et al., 2014)
	Poly (ethylene glycol) (mPEG) capped with a primary amino group	Adriamycin	Grafted; diselenium bonds instead of disulfur bonds were used to cross-link and synthesize new compounds, which had a better embedding load rate, stability and glutathione (GSH) response capability. This could help accelerate the release of embedded substances at the targeted site.	(Chen, Gao, Lü, Chen, & Liu, 2016)
β-CD	Co-precipitation and freeze-drying	Trans-anethole (AT)	The obtained β-cyclodextrin solid complex had good thermal stability while controlling the slow evaporation of AT.	(W. Zhang, et al., 2015)
β-CD	Co-precipitation method	Antibacterial polylactic acid (PLA) and cinnamon essential oil (CEO)	First, the CEO/β-CD-IC complex was prepared using co-precipitation, followed by the preparation of the PLA/CEO/β-CD-IC nanofilm using electrostatic spinning technology. This film was used for pork packaging, which had very good antibacterial effects against *E. coli* and *Staphylococcus aureus*.	(P. Wen, et al., 2016)
β-CD	Non-thermal spraying - freeze-drying (SFD)	Vanillin	Preparation of microcapsule complexes using SFD exhibited better thermal stability than spray drying and freeze-drying techniques.	(Hundre, Karthik, & Anandharamakrishnan, 2015)
β-CD	High-pressure homogenization method	Kenaf (*Hibiscus cannabinus* L.) seed oil	Sodium caseinate (SC), Tween 20 (T20) and β-cyclodextrin (β-CD) were used as emulsifiers for preparing stable nano-emulsions.	(Cheong & Nyam, 2016)
α-CD, β-CD	Freeze-drying Method	Trans-cinnamalde hyde against	Substances embedded in β-CD exhibited better antibacterial activity against *Staphylococcus aureus* and *Escherichia coli* than substances embedded in α-CD.	(Chun, Jo, Bjrapha, Choi, & Min, 2015)
α-CD, β-CD	High-speed cutting method	Wheat germ oil (WO), olive oil, coconut oil, rice	Changing the ratio of oil to CD produced non-spherical Pickering emulsion droplets, such as disc-shaped, oval and rod-shaped	(Wu, et al., 2016)

		bran oil, rapeseed oil and castor oil (CO)	droplets. Excessive microcrystals led to more stable non-spherical, rather than spherical, droplets.	
α-cyclodextrin (α-CD), β-cyclodextrin (β-CD), Hydroxypropyl β-cyclodextrin (HP-β-CD), Random methylated β-cyclodextrin (RAMEB), Low-methylation-β-cyclodextrin (CRYSMEB) andγ-cyclodextrin (γ-CD)	Freeze-drying method	Estragole (ES) and tarragon essential oils (EOs)	The obtained β-cyclodextrin solid complex was light insensitive and antioxidant active, and its release was controllable.	(Kfoury, Auezova, Ruellan, Greige-Gerges, & Fourmentin, 2015)
Hydroxypropyl □ cyclodextrin (HP-β-CD)	Hydroxyalkylated cyclodextrins	Carvacrol or monoterpene alcohols	Chitosan infiltrated HP-β-CD and glycerol-encapsulated (carvacrol or monoterpene alcohols) to produce antibacterial films that acted on *Staphylococcus aureus* and *Escherichia coli*. The relative humidity of the environment controlled the rate of release of antimicrobial substances.	(Higueras, López-Carballo, Gavara, & Hernández-Muñoz, 2016)
Water-soluble quaternized β-CD grafted with chitosan (QCD-g-CS)	Ionized cyclodextrin	Eugenol and (−)-menthol	Eugenol and (-)-menthol could self-assemble with QCD-g-CS; eugenol had a slower sustained release rate than (-)-menthol.	(Phunpee, et al., 2016)
Inulin	Alkenyl succinic anhydride with different olefinic lengths (C8-C18)	Water-insoluble active compounds	Alkenyl chrysanthemums with different degrees of polymerization were synthesized by alkenyl succinic anhydride with different olefinic lengths in aqueous solution via hydrophobic modifications. The critical aggregation concentration (CAC) and hydrodynamic diameter of the derivatives were proportional and inversely proportional to the chain length, respectively. All derivatives were capable of producing micellar aggregates and oil-in-water emulsions that provided good storage stability in the presence of Tween 20.	(Han, Ratcliffe, & Williams, 2015)
	2-octen-1-yl-succinic anhydride and 2-dodecen-1-yl-succinic anhydride (DDSA)	Medium-chain triglycerides (MCT)	DDSA-inulin in the resulting emulsion gave a smaller droplet size than OSA-inulin and had higher storage stability. The self-assembly force was mainly achieved by the electrostatic repulsion of the carboxylate ion of the derivatives.	(Kokubun, Ratcliffe, & Williams, 2015)
	OSA	No	The antibacterial activity of octenyl succinic anhydride-modified inulin (In-OSA) against *Staphylococcus aureus* and *Escherichia coli* was mainly caused by In-OSA damaging proteins and nucleic acids on the surface of bacteria, which resulted in the leakage of these two bacteria through the cell membrane and cell wall.	(X. Zhang, et al., 2015)
	Lauryl carbamate	Paclitaxel (PTX)	Modified inulin and PTX (amphiphilic compounds) could self-assemble to form micelles to improve their blood compatibility and stability, reducing cytotoxicity and	(Muley, Kumar, El Kourati, Kesharwani, &

			maintaining an effective dose of PTX for a longer period.	Tummala, 2016)
	Ethylenediamine (EDA) and pentynoic acid (P)	Doxorubicin (Doxo)	Adriamycin and pentanoic acid inulin could assemble to form a polymerizable amphiphilic complex with pH sensitivity. The net charge of the complex changed from negative to positive at 5.5 <pH <6.4, which allowed changes in its conformation and biological behaviors and released free doxorubicin.	(Mauro, et al., 2015)
	Amino-pyridines	No	Inulin derivatives had better oxidation resistance and water solubility than inulin. Their capability for cleaning was related to the position of the pyridine amino groups grafted to the inulin derivatives.	(Y. Hu, et al., 2014)
	Ammonium persulfate	D-Limonene (4-isopropenyl-1-methylcyclohexene)	Ultrasonic homogenization was used to form a highly stable Pickering emulsion consisting of nano-microcrystalline cellulose and D-limonene.	(C. Wen, Yuan, Liang, & Vriesekoop, 2014)
	Cold phosphoric acid	Soybean oil	Sodium caseinate together with regenerated cellulose nanoparticles functioned as emulsifiers to stabilize emulsions. Proteins combined with polysaccharides could reduce interfacial tension and enhance the thickness of the adsorbed layer of the surrounding fat globules to improve the stability of the emulsion system. In O/W emulsions, regenerated cellulose could improve the adsorption of the droplet onto the surface and reduce the interactions among droplets. The effect was better than microcrystalline cellulose.	(H. Hu, et al., 2016)
Cellulose	No	Lysozyme (LZ) and pectin	Electrospinning allowed positively charged lysozyme and negatively charged pectin to be alternately deposited onto the surface of the cellulose nanofiber pad via layer-by-layer self-assembly. This fiber (the outermost layer is lysozyme) had a strong inhibitory effect on *Escherichia coli* and *Staphylococcus aureus*.	(T. Zhang, et al., 2015)
	No	Chitosan (CS) and lignin sulfonate (LS)	Chitosan and lignosulfonate were superimposed on the surface of the fiber via layer-by-layer self-assembly. The anticoagulant activity of *Escherichia coli* was best when the outermost layer was chitosan, and the antioxidant activity was also improved.	(H. Li & Peng, 2015)
	No	Caffeine and chlorhexidine digluconate (CHX)	Caffeine and chlorhexidine digluconate underwent controlled release in the carrier of cellulose nanofibers (CNFs). Interactions among CNF nanoporous networks, embedded molecules and nanofibers slowed the release of molecules.	(Lavoine, Guillard, Desloges, Gontard, & Bras, 2016)
Pectin	Natural agitation or freeze-drying	Tolbutamide	Pluronic, Tween and sodium lauryl sulfate were used as surfactants to control the dispersibility and pH release properties of pectin hydrogels in water, and the release properties were good. Two different strategies were developed: blending with agarose (natural) and freeze-drying. Agarose was added to increase the embedding system of the	(Marras-Marquez, Peña, & Veiga-Ochoa, 2015)

			gel network. Freeze-drying produced a porous structure that accelerated the immersion of water, and the freshly prepared blend had a slower release rate.	
	Agitation and mixing method	Liposome	Among LM, HM and AM pectin, LM and HM pectin were the best choices for stabilizing liposomal systems. HM pectin, due to having the greatest hydrophobicity, lowest charge density and more branched structure, could encapsulate liposomes in the form of long tails and/or rings to form a larger adsorbent layer. The interaction between liposomes coated with HM pectin and mucin was the most pronounced, which could improve the adhesion to intestinal mucosa.	(Smistad, Bøyum, Alund, Samuelsen, & Hiorth, 2012)
	Co-precipitation method	Calcitonin (eCT)	Pectin-liposomal nanocomposites (PLNS) could increase calcitonin absorption in the intestine (ECT). Highly esterified PLNS with a highly negative charge ratio exhibited lower DE. Low-DE pectin PLNS showed strong mucoadhesive properties. Low-DE pectin PLNS remained at the site of mucosal adhesion after 6 hours of administration. Pectin adhered to the mucus layer and to the intestinal mucosa to extend calcitonin retention at the mucosa, especially in the duodenum and jejunum.	(Thirawong, Thongborisute, Takeuchi, & Sriamornsak, 2008)
	Ionic gelation method	Curcumin	Curcumin encapsulated by low-ester pectin beads prepared by SOLUTOL was rapidly released in an amorphous form. Curcumin encapsulated by low-ester pectin beads prepared by sodium caseinate could not be dissolved during the encapsulation process, which was related to its casein micelles.	(Nguyen, Winckler, Loison, Wache, & Chambin, 2014)
	Granulation method and an enteric coating	Piroxicam	Transcrackers prepared by Transcutol exhibited pH-dependent release in simulated gastric fluid, simulating slower intestinal fluid. Zinc-pectin/alginate beads prepared by the Piroxicam loading delivery system could extend the drug release time.	(Auriemma, et al., 2013)
	Polyelectrolyte self-assembly method	The functional agent vitamin C (Vc)	Bovine serum albumin (BSA) and citrus pectin could self-assemble to form a pH-responsive natural hydrogel (BSA-Pectin Gel, BPH). This hydrogel could carry Vc via electrostatic and covalent interactions between hydrophobic groups of BAS and amide groups of pectin.	(Peng, et al., 2016)
Chitosan	Ionic gelation method	Nisin	Chitosan nano-capsules loaded with nisin and its antibacterial activity in tomato juice was studied. Through the observation of bacterial activity in tomato juice for 6 months, it was found that chitosan nano-capsules loaded with nisin could effectively inhibit the biological activity of *Pseudomonas aeruginosa* and, to a certain extent, extend food's shelf life.	(Chopra, Kaur, Bernela, & Thakur, 2014)
	Thin-layer dispersion method combined with micro-fluidization	Vitamin C	Positive chitosan (CH) and negative sodium alginate (AL) were added to the surface of anionic nanoliposomes (NLs). After 90 days of storage, this self-assembled compound	(W. Liu, et al., 2017)

		could delay lipid peroxidation and vitamin C release at 4°C.	
High-pressure homogenization method	Papain	A stable complex was made through electrostatic interactions among hyaluronic acid (HA)/chitosan (CS) and papain, which have been shown to be a suitable enzyme delivery system in emulsions.	(Zhao, et al., 2015)
Freeze-drying method	5-fluorouracil (5-FU)	5-fluorouracil (5-FU) nanoparticles were provided based on β-glycinin (7S) and chitosan (CS). Nanoparticles were mainly formed by electrostatic interactions between amine groups (interacting NH^{3+}) of CS and 7S carboxyl groups (-COO- and intermolecular hydrogen bonds). 5-FU release was pH-dependent, which is in accordance with the Fick diffusivity of the Ritger-Peppas model.	(Y. Liu, Liang, Wei, Liu, & Liao, 2015)
Layer-by-layer self-assembly using freeze-drying method	Epigallocatechin gallate (EGCG)	CS and catechin (EGCG) double-layer composites or CS-rectorite (REC) composites (CS-REC) and EGCG double-layer composites can be self-assembled through layer-by-layer (LBL) self-assembly manufacturing technology. CS and EGCG can increase the contact time on the surface of adsorbent materials to inhibit *Staphylococcus aureus* and extend the EGCG release time.	(Tian, et al., 2016)
Polyelectrolyte self-assembly method	Tea catechins	Nanoparticles were assembled by pH-responsive chitosan and poly (γ-glutamic acid) (γ-PGA) for delivery of tea catechins. These nanoparticles improved the delivery capacity of EGCG in the cell monolayer due to their ability to tightly connect to Caco-2 cells.	(Tang, et al., 2013)
Electrofiber technology	HTCC	Positively charged N-[(2-hydroxy-3-trimethylammonium) propyl] chitosan chloride (HTCC) and negatively charged soy protein isolate (SPI) were self-assembled via a layer-by-layer mechanism on cellulose acetate (CA). The antibacterial effect of nanofiber mats was positively correlated with the number of double-layers on CA, which had a good antibacterial effect against *Escherichia coli* and *Staphylococcus aureus* (mainly by HTCC).	(Pan, et al., 2015)
Micro-phase separation method	β-Carotene (β-C)	Amphiphilic chitosan-graft-poly (lactide) (CS-g-PLA) copolymer was synthesized via homogeneous ring-opening polymerization (ROP) in ionic liquid. This significantly improved the stability of β-carotene and antioxidant activity.	(Ge, et al., 2015)
Thin-film evaporation method	Carotenoids, lycopene, β-carotene, lutein and canthaxanthin	Chitosan was adsorbed onto the surface of liposomes by electrostatic and hydrophobic forces, maintaining the spherical shape, inducing a charge reversal, enhancing the orderly distribution of the polysaccharides in the polar region and the hydrophobic core of lipid, and limiting the free movement of lipid molecules. This enhanced the stability of carotenoids under heating, gastrointestinal stress and centrifugal sedimentation conditions. The protective effects of β-carotene and lutein were best.	(Tan, Feng, Zhang, Xia, & Xia, 2016)

	Freeze-drying method	*Mentha piperita* essential oils	Chitosan-cinnamic acid could embed *Mentha piperita* essential oil to enhance its stability and antimicrobial activity against *Aspergillus flavus*. Moreover, 1000 ppm nano-gel on the surface of fruit could inhibit the growth of bacteria on the tomato surface.	(Beyki, et al., 2014)
	Ultrasonic method	Thyme essential oils	Chitosan and benzoic acid nanogel (CS-BA) could embed thyme essential oil to enhance its stability and antimicrobial activity against *Aspergillus flavus*. Moreover, 700 mg/L nano-gel on the surface of fruit could inhibit bacterial growth on the tomato surface.	(Khalili, et al., 2015)
	High-speed cutting method	Curcumin and Medium-chain triglyceride (MCT)	Curcumin was successfully encapsulated in CS-TPP nanoparticles and had good stability and sustained release in the Pickering emulsion system over a long period of time.	(Shah, et al., 2016)
	Ionic gelation method	Red ginseng extract (RG)	Fucoidan itself had anticoagulant activity, and a nanoparticle in the form of an ionic gel composed of fucoidan and chitosan helped enhance the anti-thrombotic activity of red ginseng extract in mice while improving the poor bioavailability of oral ginsenosides.	(E. S. Kim, Lee, & Lee, 2016)
Fucoidan	Ion cross-linking method and freeze-drying method	Curcumin	O-carboxymethyl chitosan (O-CMC) and fucoidan formed a pH-sensitive nanoparticle, which then encapsulated curcumin. This nanoparticle had a 92.8% encapsulation degree, and the complex was stable under acidic conditions. Under alkaline conditions, the complex could reduce cytotoxicity after release and enhanced the uptake capability of cells.	(Y.-C. Huang & Kuo, 2016)
	Agitation and mixing method	Doxorubicin	Nanoparticles formed by fucoidan and a cationic polypeptide (protamine) could be released by enzymatic digestion in an acidic intracellular microenvironment (pH 4.5-5.5). P-selectin-induced endocytosis could improve a metastatic breast cancer cell line system.	(Lu, et al., 2017)
	Ultrasonic method	Poly-l-lysine	Hollow multilayered nano-capsules were formed by chitosan and fucoidan in a layer-by-layer manner. The encapsulated poly-l-lysine was released in accordance with Fick's diffusion law at pH 7.	(Pinheiro, et al., 2015)
	Solvent evaporation method	Curcumin	The cumulative release of curcumin in a *κ*-carrageenan vector was 78% at pH 5.0, which thereby induced a decline in the mitochondrial membrane potential of cancer cells and eventually resulted in apoptosis.	(Sathuvan, et al., 2016)
κ-Carrageenan	Agitation and mixing method	Curcumin	*κ*-carrageenan and lysozyme self-assembled to form a micro-complex and embed curcumin. The solubility of the complex increased significantly, and the stability increased by approximately 2.7-fold, 2-fold and 1.7-fold compared to un-self-assembled curcumin, respectively, which could maintain its biological activity after Pasteurization and ultraviolet radiation.	(W. Xu, et al., 2014)
Alginate	Agitation and mixing method	Curcumin	The prepared alginate-curcumin (Alg-Ccm) conjugate had great solubility and stabilization in water at pH 7.4, and the cytotoxicity remained.	(Dey & Sreenivasan, 2014)
	Agitation and mixing	β-lactamase	Sodium alginate (Alg) and lysozyme (Lyz)	(Fuenzalida, et

	method	(BLA)	formed a nanopolymer electrolyte complex, and the addition of Alg molecular weight or Ca^{2+} resulted in higher cross-linking with Lyz, the associated second enzyme BLA. The activity was related to the ionic strength of the solution.	al., 2016)
Sodium alginate	Dynamic high-pressure microfluidization (DHPM)	Nanoliposomes	A polyelectrolyte delivery system (PDS) based on sodium alginate (AL) and chitosan (CH) coated on the surface of nanoliposomes (NLs) was prepared, which could resist lipolytic degradation under simulated gastrointestinal conditions.	(W. Liu, et al., 2013)
	Ultrasonic method	α-amylase	Superparamagnetic carboxymethyl chitosan/sodium alginate nanosphere (SM/CMC/SA) could fix α-amylase and increase enzymatic activity by 4.67-fold as well as its stability against acid, alkali, heat and storage conditions.	(J. Jiang, Chen, Wang, Cui, & Wan, 2016)
	Agitation and mixing method	Vitamin C	A polymer of liposomes (LPs), chitosan (CH) and sodium alginate (AL) had the ability to reduce the release of vitamin C from simulated intestinal fluid. The release rate was highest after mixing with pancreatic and bile salts.	(W. Liu, et al., 2016)
	Agitation and mixing method	Potential lipophilic agents	Sodium alginate and whey protein isolate (WPI) self-assembled to form a soluble biopolymer complex. At high temperature, more hydrophobic groups were exposed on the surface of the whey protein isolate, which benefited the interactions between the complex and potential lipophilic bioactive agents.	(Fioramonti, Perez, Aringoli, Rubiolo, & Santiago, 2014)

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hydrogen bonding interactions between EDTMP and chitosan result in the coacervation of chitosan. (iii) The coacervation of chitosan results in the in situ encapsulation of Hb. (iv) The interaction between EDTMP and Hb facilitates the encapsulation of Hb.

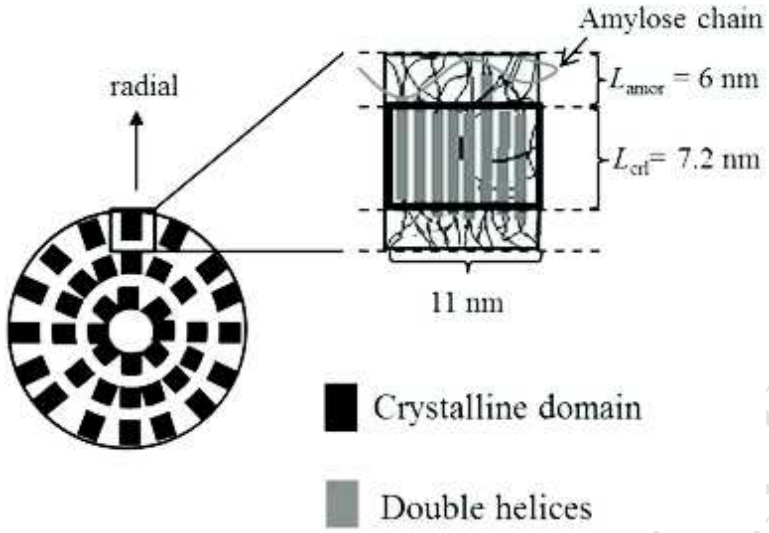

Fig. 1. Schematic model of the radial positive organization of debranched waxy rice starch (DNRS) spherulites. The arrows indicate the radial direction of the spherulite.

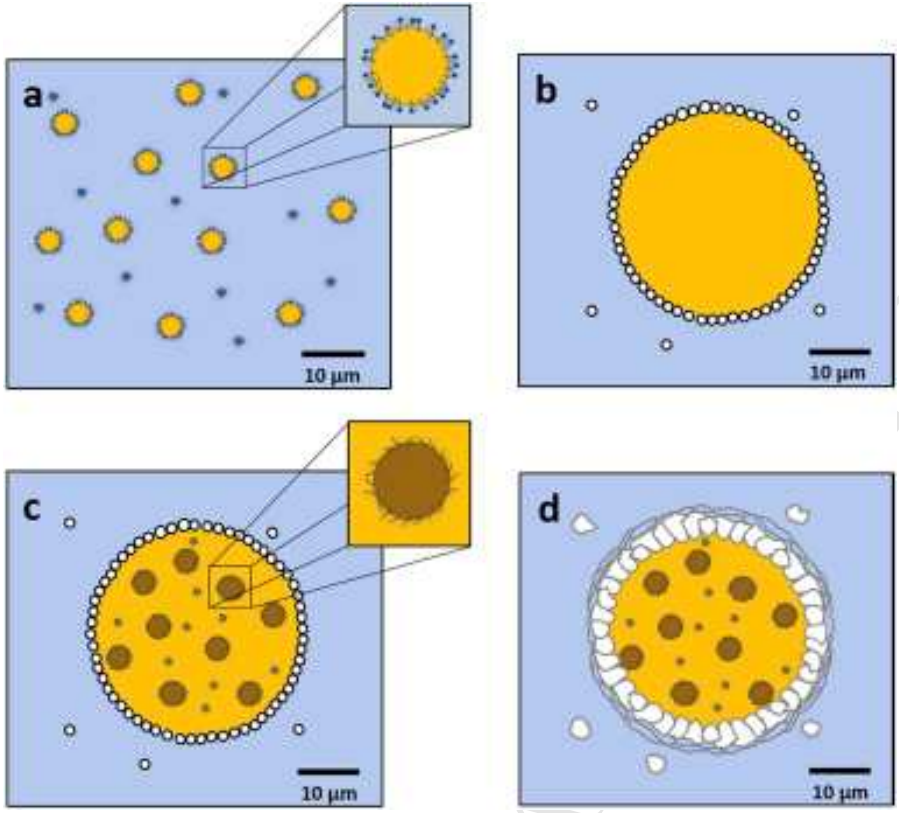

Fig. 2. Schematic representation of different types of emulsions: (a) surfactant-stabilized emulsion, (b) particle-stabilized emulsion, (c) starch granule-stabilized double emulsion and (d) heat-treated starch granule-stabilized double emulsion.

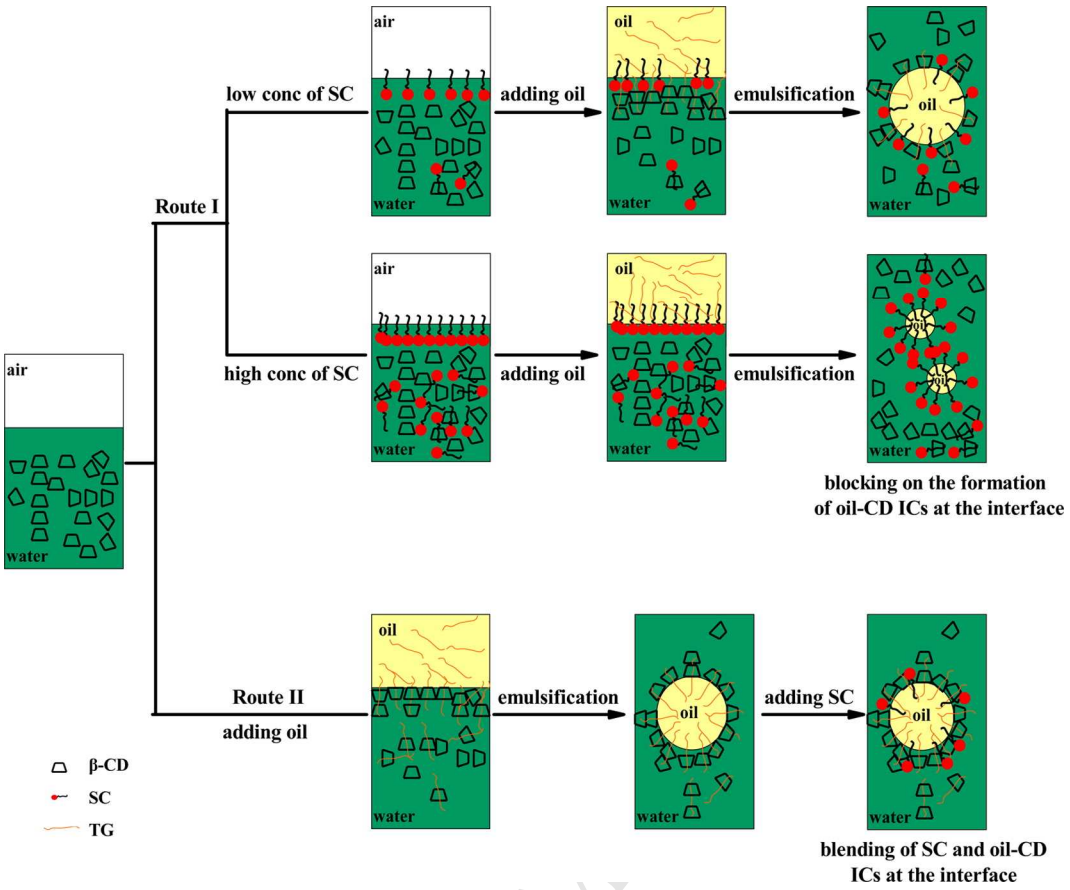

Fig. 3. Schematic representation of the assembly model for the β-CD (used as solid colloidal particles)/SC (sodium caseinate, used as an emulsifier)/TG (triglyceride) system at the oil/water interface (H. Xu, et al., 2015).

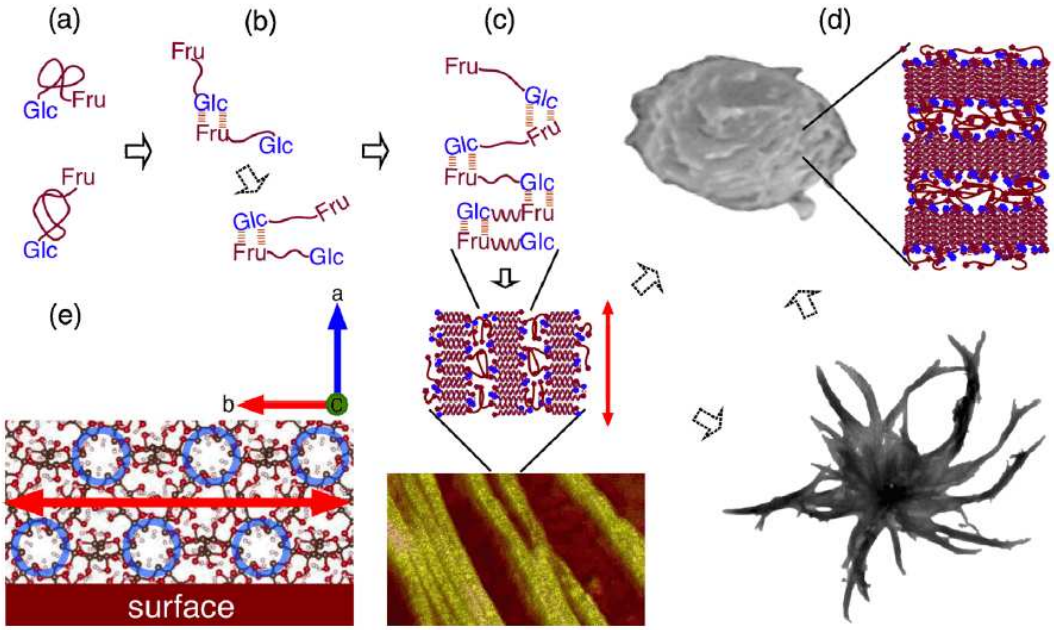

Fig. 4. Schematic representation of inulin particle formation: (a) inulin chains with random coils; (b) formation of glucose–fructose links; (c) antiparallel arrangement of inulin helices in ribbons (arrow indicates the long axis of the ribbon); (d) inulin ribbons combined, likely through spherulite intermediates, forming semicrystalline particles; (e) inulin ribbons lying flat on a surface (rings accentuate inulin helices).

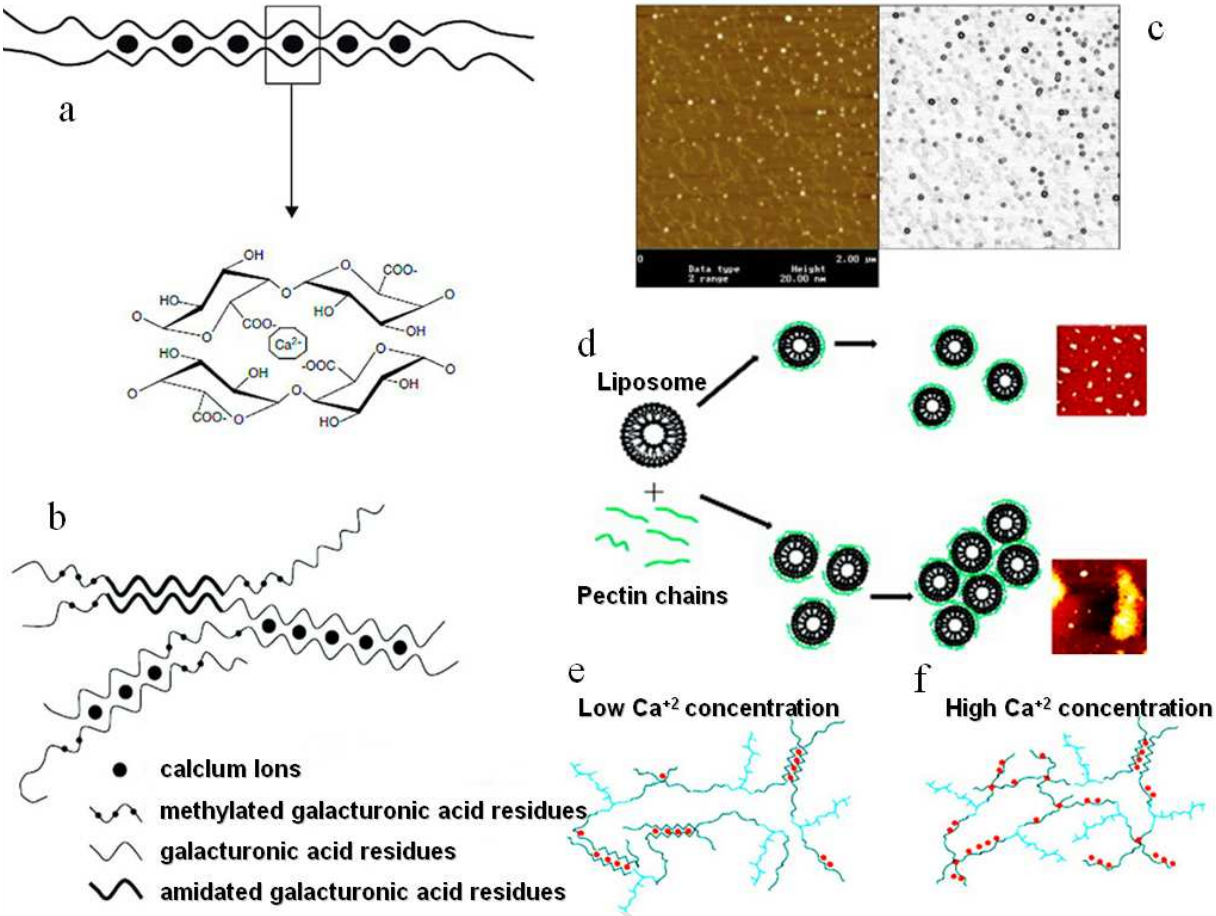

Fig. 5. Schematic representation of (a) calcium binding to polygalacturonate sequences of LM pectin ('egg box' dimer and 'egg-box' cavity) and (b) a model for the gelation of amidated LM pectin; (c) topographical (left) and equivalent processed (right) images from atomic force microscopy (AFM) of pectin–liposome nanocomplexes (PLNs) using pectins; (d) different proportions of liposomes and pectin interactions; (e) calcium–pectin gel with low calcium concentration; (f) calcium–pectin gel with high calcium concentration.

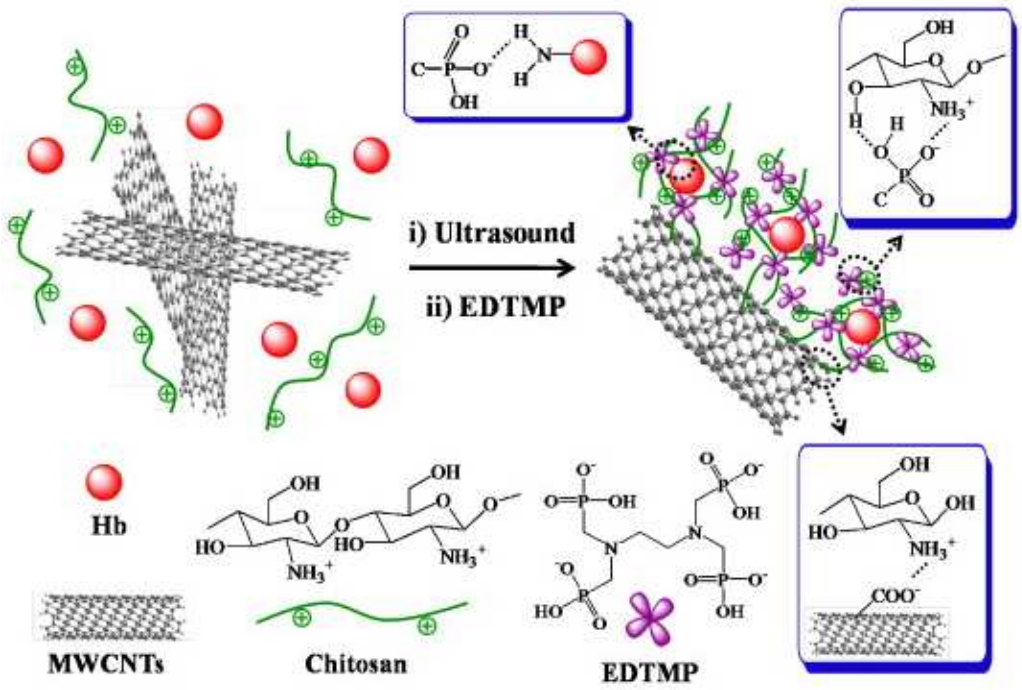

Fig. 6. Schematic illustration of the synthetic process and mechanism of EDTMP–Hb–chitosan–MWCNT composites. Key points: (i) The interaction between chitosan and MWCNTs results in the dispersion of MWCNTs. (ii) The strong electrostatic and/or hydrogen bonding interactions between EDTMP and chitosan result in the coacervation of chitosan. (iii) The coacervation of chitosan results in the in situ encapsulation of Hb. (iv) The interaction between EDTMP and Hb facilitates the encapsulation of Hb.

Highlights

- The activity of bioactive compounds is limited due to their instability.
- An overview of delivery systems based on various carbohydrates is provided.
- The assembling food ingredients using carbohydrate biopolymers is reviewed.
- The protective effects of the corresponding delivery systems are highlighted.

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